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Germany, Denmark, Spain, France,
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The Netherlands and Sweden**

㉕ Applicant: **RÖHM GmbH**

**Kirschenallee
D-64293 Darmstadt (DE)**

㉖ Inventor: **Krieg, Manfred, Dr.**

**Kesselhutweg 19
D-64289 Darmstadt (DE)**

Inventor: **Iltman, Günther**

**Waldstrasse 15
D-64823 Gross-Umstadt (DE)**

㉗ **Molten polymethyl metacrylate mold production process for high-speed filling.**

㉘ The invention deals with a filling mold production process in a polymethyl metacrylate base through mass polymerization, within its own polymerization chamber, where by known means, an initial fluid PV polymeric phase is produced containing monomer, where, by high-speed agitation during the formation of an SP suspension, the FS particulate filling material is introduced in the proportion from 30 to 80% in weight in relation to the formed SP suspension, and where, shortly before filling the polymerization chamber, a radical initiator and solid particulate PP polymer, in the proportion from 1 to 20% in weight in relation to the SP suspension, is added to the SP suspension, with a homogenous distribution, and then introduced into the polymerization chamber and then polymerization is performed and mold removal is made.

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Purpose of the Invention:

The invention deals with a process for producing cast PMMA molds for high-speed filling.

State-of-the-Art

Traditionally, through the mass polymerization method transparent metacrylate plates are produced, the so-called "cast PMMA plates" (compare H Rauch-Puntigam, Th. Völker, Acryl- und Methacrylverbindungen, Springer-Verlag 1967, pg. 275-292). On a par with transparent "acrylic glasses", the filling material, of prevalingly inorganic nature, doped with acrylic resin has experienced growing importance, especially in the sanitary area, kitchen, as decoration plates, etc. Acrylic glass doping is done with polymeric particles. Thus, in DE-A 35 28 165 pearls interconnected with dense plastic elements are described. DE-A 42 16 341 recommends PMMA molds with light dispersal, which are obtained by adding, among others, particles containing interconnected phenolic groupings. And, further, an acrylate plastic production process is described with differentiated surfaces by means of colors by applying colored polymer pearls in DE-A 31 10 093. Likewise, electricity conducting plastics are described, whose conductivity is based on the presence of doped polymeric particles with conducting surfaces (DE-A 35 43 301). At first, the proved technology utilized in production with filling material doping, the so-called "high-speed filled" plates, is apparently applicable for PMMA transparent plate production. US-A 3 706 825, describes, for example, a production process imitating high-speed filled marble in continuous mode using and extruder.

Objectives and Solution

Problems and objectives that in general are to be resolved in cast high-speed filling molds are presented as follows based on cast and filled plate production. This is how it is with cast, filled PMMA plates, obtained by the direct application of the up to the present unsatisfactory production method. In order to speed up the polymerization process, the REDOX systems technique is often used for initiators (compare Rauch-Puntigam et al. loc.cit.). The application of this method for producing plates with high-speed doping faces multiple problems.

It is observed, in the production of thicker plates (for example 10-20-mm thick) with large sizes, that polymerization already occurs during the filling operation, that a controlled polymerization in the standard shape for such destination, is no longer admissible. In this manner, strains on the plates and consequent stretching are resulting from uncontrolled tensions during the polymerization process.

In "slower" polymerization (2 to 3 hours go by in water-bath) such strong sedimentation of relatively thick filling material occurs that ready plates do not become homogeneous and are clearly presented curved. Furthermore, sedimentation cannot be completely removed by using syrup containing polymer.

Therefore, it deals, at first, with a "slow" polymerization, and it was then necessary to remove presented problems, especially the unavoidable sedimentation observed with plate curving caused by this procedure.

Therefore, the objective is to make a process available for producing filled PMMA molds, so that described deficiencies can be prevented, keeping basic technical premises.

This objective is achieved in the best manner with the process object of the invention.

Thus, the invention deals with a process for producing filled molds based on polymethyl metacrylate through mass polymerization in own polymerization chamber, where, by an already known method, an initial fluid PV polymeric stage containing monomers is produced, in which the particulate inorganic filling material in the proportion of 30 - 80% in weight in relation to the formed SP suspension is introduced by high-speed agitation during the formation of an SP suspension and where a radical initiator, or then, an initiator system, a particulate solid PP polymer, preferably, also from PMMA in the proportion of 1 to 20 parts in weight in relation to the SP suspension prepared for polymerization shortly before filling the polymerization chamber.

Initial PV stage monomers have, at least from 50 and 100 % in methyl metacrylate weight, in par with other suitable alkylesters or ariloesters, (met)acrylic acid, with, generally, 1 - 8 carbon atoms, such as for example ethyl (met)acrylate, propyl (met)acrylate, butyl (met)acrylate, or then, isomers, ethylexile 2-(met)acrylate, cyclohexile (met)acrylate, phenyl (met)acrylate, benzyl (met)acrylate, used as comonomers.

Furthermore, initial polymeric stages may further contain known intertwined monomers, for example, those with at least two vinyl groups suitable for polymerization in the molecule (compare Rusch-Puntigen,

"Acryl-und Methacrylverbindungen", page 164, Springer-Verlag, 1976), which mentions examples with dimetacrylate and ethylene glycol acrylate, 1,4-dimetacrylate and butanediol acrylate, dimetacrylate and triglycol acrylate, dimetacrylate and trimethylpropane acrylate, alile composites such as alile metacrylate or trialile cyanide. The intertwined monomer content has, usually, from 0.1 to 1.5% in weight in relation to monomers. In addition to monomers, the initial PV polymeric stage contains, preferably, a PM pre-polymer in the proportion from 1 to 15% in weight in relation to the initial PV polymeric stage.

As PM pre-polymers, we have, for example, used pertinent PMMA polymers, which, when applicable, may contain less expressive proportions of up to about 15% in weight of pertinent selected comonomers, such as, for example, methyl acrylate. As a rule, pre-polymers have a molecular mass in the range from 2×10^4 up to 4×10^5 daltons [determined according to Size Exclusion Chromatography (SEC)]

This invention observes the principles of the state of the technique in relation to the initial PV polymeric stage, (for example, DE-PS 24 49 656, EP-PS 0 214 551 or EP-PS 0 218 866), so that the initial fluid polymeric state presents a viscosity lower 5 Pa-s, preferably, lower than 0.5 Pa-s, at the temperature foreseen for casting.

As FS filling material pertinent finely particulate inorganic or organic materials used for casting resin are suitable. The particle can be colorless or pigmented. In this manner a 200µm diameter should not be exceeded, preferably, 60µm. Furthermore, filling materials with larger particles can also be used for special purposes, for example, up to about 10% in weight in relation to the SP suspension. When using cristobalite as filling material, it should preferably have, at least, a <10µm size, 95% of particles. Particles with a $\approx 0.1\mu\text{m}$ size, should not, to the extent possible, exceed 10% of total particle number. Particle granulometry observes usual methods (see B.Scarlett in "Filtration & Separation", page 215, 1965). Particle size determination will be based on larger particle sizes, respectively. Preferably, particles are granuliform. Eventually, it may be advantageous, to release the particle from inherent absorbing moisture by heating to about 150 °C. FS filling materials can be produced with natural or synthetic products. Mechanical properties such as hardness, transversal elasticity module, are determined according to the application foreseen for the casting resin. By this, a transversal elasticity module with a setpoint lower than 5GNm⁻² may be advantageous. For example, minerals such as aluminum oxide, aluminum hydroxide, or then aluminum oxide hydrate and byproducts, for example, are suitable:

2-alkaline soil oxide and alkaline soil hydroxide, clays, silicon dioxide in their various modifications, silicate, aluminum silicate, carbonate, phosphates, sulphate, sulphides, oxides, coals, metals, and metal alloys, preferably in the shape of foil or sequin.

Furthermore synthetic materials are suitable, such as glass powder, ceramics, porcelain, slags, finely granulated SiO₂. Silicon acid, such as quartz (post quartz), tridimite and cristobalite are also appropriate, as well as kaolin, talc, mica, feldspar, apatite, barite, plasters, chalk, limestone, dolomite. If such is the case, filling material mixtures can be used. The proportion of filling material contained in the SP Suspension (containing filling material), preferably, and, at least, 40% in weight. Generally an 80% proportion in weight is not exceeded. The indicated content value is the SP suspension filling material content of >50 to 80% in weight. Filling material production with suitable granulometries can be achieved by known methods, for example, by grinding and milling. Especially, cristobalite is preferable together with aluminum hydroxide. Preferably, the inorganic filling material will be obtained so that the hardened resin will have a transversal elasticity module of, at least, 5GNm⁻², preferably, with less than 10GNm⁻², and should, when configuring mechanical properties, be considered the foreseen utilization for casting resins.

In a preferential execution manner, average particle granulometry is in the 60 - 0.5µm range, preferably, the hardness content (according to Mohs: see. Römpf's Chemie-Lexikon, 9th Edition, page 1700, Georg Thieme Verlag, 1990) of FS filling material, in the case of cristobalite, is 10, in the case of aluminum hydroxide 2.5 - 3.5. Si-M silane agent is employed, in the known form, as an adhesive agent between the filling material and the organic phase. Whereby, already known organosilicon composites can be used from the state-of-the-art [see D. Skudelny Kunststoffe 77, 1153 - 1156 (1987); Kunststoffe 68 (1978); Firmenschrift Dynalisan® , Haftvermittler der Dynamit Nobel Chemie].

Before anything else, it deals with organosilicon composites with, at least, one molecule unsaturated ethylic group, is in general connected to the central silicon atom through Atom C. The other silicon connectors are, as a rule, alcoxide residues with 1 to 6 carbon atoms (when ether bridges are still found in the alkyl residue). Vinyl trialcxisilane must be mentioned, for example. The double CC connection can also be connected with Si atom through one or more carbon atoms, for example, in the form of alile trialcxisilae or metacryloxipropyl y-trialcxisilane. Dialkoxisilae can also be used, where another functional residue is connected to Si atom with a double CC connection, in general of the same type, or an alkyl residue with, preferably, 1 to 6 carbon atoms.

There may also be different kinds of organosilicon composites in organosilicon components. Among them, for example, vinyl trimetoxysilane, vinyl triethoxysilane, vinyltris (methoxy ethoxy) silane, divinyl dimetoxysilane, vinyl methyl dimetoxysilane, vinyl trichlorosilane, β -metacycloxypropyltrimetoxysilane β -metacycloxypropyltris-(methoxyethoxy)-silane. Preferably, organosilicon composites are used with amine catalysts, especially of the type for alkylamine, with 3 to 6 carbon atoms, especially used with n-butylamine. The content value for using amine catalysts may be from 0.05 to 10% in weight, preferably, from 1 to 5% in weight, of organosilicon components.

Generally, the organic filling material weight proportion in relation to the organosilicon composite is from 500: 1 to 20:1, preferably, 50 : 25 : 1. It is of vital importance for the process object of the invention that the particulate solid PP polymer be added to the formed SP suspension and prepared for polymerization.

The particulate PP polymer is, preferably, an acrylic resin, especially PMMA, or then an MMA copolymer, for example, such as monomers destined for the initial PV polymer (see above), or then, other suitable vinylic monomers, generally in the proportion of 20% in weight, in relation to PP polymers, especially in the amount of 0.2 - 15% in weight (see Ullmanns Enzyklopädie der Technischen Chemie, 3rd Edition, Vol. 14, pages 108 to 110, Urban & Schwarzenberg, 1963), such as, for example, vinyl ester and vinyl ether, as well as vinyl composites, carbon vinylic composites, vinyl aromatics, vinyl heterocyclic composites and similar. Polymers forming PP particles have, in general, in intertwined condition, a molecular weight in the 10000 to 2 000 000 dalton range.

If such is the case, polymers may also contain monomers in intertwined condition, as informed for the initial PV polymeric stage, which is to say, pearls can be intertwined. The polymeric PP particle has, in general, a diameter in the 5 to 1 000 μ m range. Particularly special, preferably, are PP polymers in the shape of a pearl, especially with particles with an average granulometry from 0.02 to 0.3 mm, especially in the 0.03 - 0.15 mm range. Polymeric pearl production of a suitable type is, for example, described in DE-A 31 30 093, DE-A 21 35 828, or then, in DE-A 28 15 506. PP pearls can, in turn, be doped with filling materials and/or with coloring substances, where doping observes, as a rule, the quality and quantity of described PP suspension.

Pearl polymerization consists, as it is known, of the transformation of a little soluble monomer (or then, desalinated) in water, or then watery salt solution. In addition to the accelerator and suitable polymerization agents, suspension stabilizers are also added, for example, water-soluble protection colloids. The size of pearls, as known, essentially observes the process technical specifications, for example agitation speed, as well as the type and amount of suspension stabilizers. Generally, monomer-soluble and water-soluble initiator radicals are used, for example, dibenzoyl peroxide and lauroyl peroxide with azoic initiators. Around the end of the polymerization process, if such is the case, high-capacity decomposition agents are added (compare, Brandrup-Immergut, Polymer Handbook, 3rd edition, Chapter III, pages 1 - 65, J.Wiley, 1989), which, as a rule present a proportion of 0.1 to 1 % in weight, preferably, from 0.5% in weight, in relation to monomers.

As regulators, we have - as well as in mass polymerization from the initial PV polymeric stage - the employment of usual sulphurous regulators. Especially were proved such as aliphatic mercaptan and/or sulphuric ether. We must mention, for example, laurylmercaptane, Bis - sulphate-(2-ethylhexyle), bis sulphate-(2-mercaptoethyl) and similar. Regulator proportion is generally from 0.01 to 1.0% in weight, preferably, from 0.05 to 0.4% in weight, compared to monomers. The molecular weight (Mw) for pearls used according to the invention is, generally, 104 and 2 x 106, preferably, between 105 and 106 (determined through chromatography by gel permeation, compare H.F. Mark et al, Encyclopedia of Polymer Science & Technology, Vol. 10, pages 1 - 19, J. Wiley, 1987). Irregular or poorly intertwined pearls can also be used, if such is the case.

As suspension stabilizers water-soluble macromolecular composites can be used, such as for example, polyvinyl alcohol or polyacrylic acid in an amount from 0.01 to 1 % in weight, in relation to monomers or powdered inorganic additives, which, such as may be produced by addition or middle precipitation. We must mention here, for example, alkaline earth salts, such as carbonate, carbonate sulphate, carbonate silicate, etc. (compare C.E. Schildknecht Polymerization Processes, J. Wiley & Sons, 1977, Page 119 back). Pearl polymerization can be performed at high temperatures, for example, between 50 and 100 °C, an outlet 75°C temperature being admitted.

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Also here, temperature determination should take into account the heat resulting from polymerization. An indicator for completing the polymerization process is the exothermal reaction reduction, that is, temperature drop after reaching maximum temperature. In the manner of this invention, a reheating occurs during a given time more or less in the reached temperature range. Instead of polymer pearls, other produced polymeric particles can also be used, with a granulometry in the 5 to 1000µm range.

Particle granulometry is determined according to the usual process, based on several larger size particles (compare B. Scarlett, Filtration & Suspension, page 215, 1965). Thus, a particulate PP polymeric material can be obtained from a solid polymer, for example, from plates, by comminution, especially grinding, up to the desired thinness grade, meeting (compare H.Rumpf, Kunststoffe 44, 43, 93 (1954); H.Balzer, Polymere Werkstoffe, Vol. II, Technologie 1, 105-111, Georg Thieme-Verlag, 1984). Grinding for example with fixed hammer mill in cross was successfully tested. Granulometric fractions can be separated in the usual manner, for example, by sieving (compare Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd edition, Vol. 21, page 114, J.Wiley, 1983.). Incorporation and distribution of particulate PP polymers in SP suspension, occurs, for the purpose of this invention, by agitation, for example, through an agitation aggregate, as a rule, in the 300 - 1000µm range.

In addition to mentioned components, usual accessory SP suspension agents, can be still added as stabilizers, ultraviolet protective agent, separation agent, anti-sticking agent and similar, and especially, coloring substances with pertinent dyes and pigments used in concentrations up to about 10% in volume, in appropriate amounts for such (compare Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. 20A, pages 459 - 507, VCH 1992). Especially, it is worth mentioning, as coloring substances, pigments yellow or then red, for example, iron oxide-based, such as, for examples, those with titanium oxide base, titanium sulphate, black pigments, for example, such as blue pigments, or then, green pigments such as those with ultramarine blue base, or then, cobalt (compare M.&O.Lückert, Pigment- und Füllstofftabellen, Laatzen 1980; H.Balzer, Polymere Werkstoff, Vol. II, pages 37 - 353, Georg Thieme-Verlag, 1984). In addition to coloring substances and pigments, other known additives are also suitable, for example, metals and their byproducts, in different shapes, especially in the shape of plates, or then, flakes, such as fibers, chips, shavings or powders, for example, of aluminum, copper, bronze, silver, gold,

brass, chrome, nickel, iron, or then, steel, tin, titanium, tungsten, zinc, in addition to non-metallic chips or flakes, for example, of titanium nitrate, nickel sulphate, magnesium sulphate.

- 5 Other flakes, fiber shavings, natural or synthetic, and similar obtained from nylon, or then, from polyamide, cotton, linen, polyester, glass, hairs, wool, hemp, paper paste, polyacrylic nitrile, polyethylene, polypropylenes, several kinds of proteins, mineral wool, ligneous fibers.
- 10 The coloring substance addition – if such is the case, of filling polymeric particles – of the above-described combination occurs in preferential execution manner. Preferably, average particle granulometry is located in the 0.01 - 2mm range. By applying pigments in the manner of this invention for example, red, yellow and/or black pigments and, if such is the case, white pigments and/or metallic pigments, a decorative stone is obtained in the mold body, for example (type: granite or marble).

20 Process Execution

In this manner, the process object of this invention with the usual initial PV polymeric state, containing methyl metacrylate, and, if such is the case, other monomers, as well as, such as, pre-polymer.

- 25 The fluid phase formed in this manner further contains, for the purposes of this invention, the SI-M silane agent. In this fluid organic phase, the inorganic filling material is then introduced during the formation of a suspension, by mechanical agitation, for example, through a solvent. The indicated content value for this process is about 10 minutes. Generally, the FS filling material addition occurs so that the organic phase viscosity does not exceed a value of about 10 Pa-s.
- 30 Alternatively to silanization in the organic phase, suspension can also be obtained with already silanized FS filling material. Next, the accessory polymerization agent is dissolved, as well as known polymerization initiators in quantities of, generally, from 0.1 to 5% in weight in relation to M monomers.
- 40 As polymerization initiators radical formers will be used, whose decomposition can be thermally induced in radicals. Basically, all those already supplying high current at low temperature are suitable (compare J.Brandrup, E.H. Immergut, "Polymer Handbook", 3rd edition, chapter III, pages 1 to 65, J.Wiley, 1989). Among others, are, for example, initiators having a one-hour semi-decomposition period at 40 - 100°C temperatures, such as, for example, butyl perpivalate terc. and peroxide bis-dicarbonate(butyl 4- cylohexile terc.).
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In the manner of this invention, the addition of initiators occurs shortly before filling casting resin suspensions, followed by adding particulate PP polymers. The addition of PP polymers to solid suspension occurs in the same manner, shortly before filling chambers in the indicated manner. If allowed by circumstances, still before PP polymer dilation for nominal value compositions. The introduction of particulate PP polymers in the suspension can, preferably, be done by mixer extruders with vacuum degassing, or then, with a double thread extruders. Preferably, the suspension is emptied before filling. By dilating PP polymers in the polymerization chamber, the viscosity, or then, the composition viscosity, is high, so that filling material sedimentation can no longer occur, or then in a safe amount.

The time needed for dilation, or, until viscosity rise, as well as viscosity rising levels, can be controlled through the molecular weight, particle granulometry and PP polymer amount.

The quick suspension gelation slows filled polymerization chambers to be idle for a long time, the time indicated for stopping is about one half to one hours, with no sedimentation occurring. In this manner, it is possible for larger units, for example, in complete manner, to be detached for polymerization.

The actual cure (=polymerization) occurs, preferably, by feeding by thermal energy, for example, water-bath, by heating at 35 - 80 °C, for example, during 20 to 300 minutes, where the cure can occur either with or without pressure application. Thus formed molded pieces, for example, polymer plates, are then, in known manner, removed from the mold. The monomer residue content of cured polymers is generally less than 1% in weight, particularly, less than 0.5% in weight in relation to monomer totality.

Advantageous Results

The process object of this invention, also allows in surprising manner producing relatively thicker PMMA plates, with sizes of approximately 4 000 x 2 500 x 20, by using state of the technique systems.

Considering that polymerization can be performed in reproducible manner according to defined conditions, it is possible to prevent the occurrence of an uncontrolled polymerization, such as, for example, tensions on the product.

As a consequence of removing sedimentation from the filling material bent, non-homogenous plates will no longer occur. The process provides – as already mentioned – multiple control possibilities allowing influencing viscosity rise in due time.

Standard equipment utilization for producing cast PMMA plates also shows to be especially.

Through it, the process also shows to be suitable for producing installations such as, for example, dishwashers, washbasins, bathtubs and shower boxes and other sanitary installations. By appropriate hot stamping a decoration with stones can also be obtained in all application modalities.

The possibility of a continuous execution mode of the process object of the invention is also worth mentioning.

EXAMPLES

Example 1

In a syrup consisting of 9.569 kg of methyl metacrylate, 950g of a polymethyl metacrylate molecular mass Mw of about 3×10^5 g/mol (PLEXIGUM® M 920 manufactured by Röhm GmbH), 1.14g of de 2.4-dimethyl-6-butylphenol terc., 114g of glycol dimetacrylate, 190g of stearic acid and 5.7g of 1-isopropyl-4-methyl-1.4-cyclohexadiene, 25270g of aluminum hydroxide are produced and dispersed, by agitation in a solvent, containing a mix with average 45μ and of 7 - 8μ granulometry particles (ALCOA C33 and ALCOA C333 Products). Then, 38g of bis-(4-butylcyclohexile terc.) peroxidicarbonate, 38g of butyl perpivalate terc. and 19g of butyl perchlorate terc. are dissolved in the suspension. After mixing 1900g of a particulate polymetacrylate with Mw = about 5×10^5 g/mol, average particle granulometry of about 50μ (PLEXIDON® M727 Product of Röhm GmbH), the deposit is emptied and introduced into a silicate chamber 12mm away. The closed chamber is heated in water-bath at 40°C during 160 minutes. Final polymerization occurs in a drying oven at 110°C during a 60-minute period. After cooling the chamber, plate casting wastes are removed. The plate has no bubbles and is not curved.

Patent Claims

1. Filling mold production process based on polymethyl metacrylate by mass polymerization in own chamber for polymerization, thus characterizing that,

according to a known method, an initial PV polymeric phase is produced containing monomers, in which FS particulate filling material is introduced in the proportion from 30 to 80% in weight in relation to formed SP suspension, by high-speed agitation during suspension formation, and where a radical initiator and a solid PP polymer are added to an SP suspension shortly before filling the polymerization chamber, in the proportion from 1 to 20% in weight in relation to the SP suspension, with identical distribution, then introduced in the polymerization chamber, being then, polymerization and mold removal performed.

2. Process according to Claim 1, where it becomes characterized that the particulate solid PP polymer is an acrylic resin. 15
3. Process according to Claims 1 and 2, where it becomes characterized that the particulate solid PP polymer contains filling material and/or coloring substances. 20
4. Process according to Claims 1 to 3, where it becomes characterized that the particulate solid PP polymer has a diameter in the 5 - 1 000µm range. 25
5. Process according to Claims 1 to 4, where it becomes characterized that the particulate solid PP polymer consists of a pearl polymer. 30
6. Process according to Claim 1, where it becomes characterized that, FS particulate filling material has particles with average granulometry in the 60 - 0.5 µm range. 35
7. Process according to Claims 1 and 6, where it becomes characterized that the FS particulate filling material is inorganic. 40
8. Process according to Claim 7, where it becomes characterized that the inorganic FS particulate filling material is an aluminum hydroxide. 45
9. Process according to Claims 1 to 8, where it becomes characterized that coloring substances are added to molds. 50
10. Process according to Claim 9, where it becomes characterized that coloring substances are added in the form of colored polymeric particles, if such is the case, also filled with granulometry in the 0.01 to 2 mm range. 55

11. Process according to Claims 1 to 8, where it becomes characterized that coloring substances are added in the form of particulate pigments.

- 5 12. Process according to Claims 1 to 11, where it becomes characterized that plates are produced as molds.
- 10 13. Process according to Claims 1 to 11, where it becomes characterized that unplanned installations are produced as mold, selected from the dishwasher, washbasin, bathtub and shower box group and other sanitary installations.



EUROPEAN REPORT ON RESEARCH

Filing Number
EP 94 11 2189

PERTINENT DOCUMENTATION			
Category	Document reference with data deemed necessary with pertinent sections where they are found.	Referring to claims	Filing classification (International Class 6)
X	WO-A-90 01470 (E.I. DUPONT DE NEMOURS AND COMPANY, INC) *Claims* *Page 4, line 1 - line 2*	1-13	CO4B26/06 CO8F2/44 CO8K3/22 CO8K3/00 A47K1/00
X	WO-A-92 03497 (ARISTECH CHEMICAL CORPORATION) *Claims* *Examples* *Page 6, line 29 - Page 7, line 3*	1-4, 6-13	A47K3/00
A	WPI DATABASE Derwent Publications Ltd., London, GB; AN 78-46522A & JP-A-53 055 357 (ASAHI CHEMICAL IND KK) May 19, 1978 *Summary*	1-7	
D, A	EP-A-0 218 866 (RÖHM GMBH) *Claims* *Examples*	1, 6-8, 12, 13	
			Technical Areas Researched (International Class 6)
A	EP-A-0 270 915 (ESPE STIFTUNG & CO PRODUKTIONS-UND VERTRIEBS KG) *Claims* *Page 2, line 8 - Page 3, line 5*	1	CO4B CO8F CO8K CO8L
This report was issued for all patent claims.			
Place of Research The Netherlands		Research Completion Date November 10, 1994	Author Persson, E
CATEGORIES OF MENTIONED DOCUMENTS			
X: of particular importance everything that has been informed Y: of particular importance in relation to another publication of the same category A: technological precedences O: no written disclosure P: intermediary bibliography T: theories or principles contained in the invention fundaments		E: old patent document that, however, was disclosed on or after filing date D: document described in the filing I: document described for other reasons *integrating the same patent office, pertinent document	